Equilibrium dec 15 file 2

Monday, December 12, 2022 3:33 PM

Doubt Step 2

~~11~~, ~~15~~, ~~12~~, ~~14~~, ~~13~~, ~~66~~, ~~69~~, 103, 51

(11) $\Delta G^\circ = -RT \ln K_p$ $\quad K_p = P_{CO_2}$

$-13.5 \times 10^3 = -2.303 RT \log(P_{CO_2})$

$R \rightarrow 8.314$ or $\frac{100}{12}$

(15) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

t=0: 1 mole → 92 g; 0

$\frac{92 \times \frac{20}{100}}{92}$ = 0.2

atm: 1 − 0.2; 0.8; 0.4

% mass diss = % mole diss

Total moles at Eq^m = 1.2

(#) $PV = nRT$ (initially)

$1 \times V = 1 \times R \times 300$

$V = 300R$

$RV = nRT$

$P \times (300R) = 1.2 \times R \times 600$

$P = 2.4$ atm

Haber's Process

(17) $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta H = -46.1$ KJ/mole

Catalyst ⇒ Scrap Fe or Fe oxide → Fe_2O_3, Fe_3O_4

Promoter (to ↑e efficiency of catalyst) ⇒ Molybdenum (Mo)

(66) $NH_4SH(s) \rightleftharpoons NH_3(g) + H_2S(g)$ → 3 L, 600 K

0.1 mole; 0; 0

0.1 − 0.1α; 0.1α; 0.1α

Total moles of Gas = 0.2α

$= 0.2 \times \frac{80}{100}$

$= 0.06$

$K_c = [NH_3][H_2S]$

$= \left(\frac{0.1\alpha}{3}\right)^2$

$= \left(\frac{0.1 \times 0.3}{3}\right)^2 = 10^{-4} = \frac{K_p}{(RT)^{\Delta n_g}}$

$10^{-4} = \frac{K_p}{(0.0821 \times 600)^2}$

(69) $A(s) \rightleftharpoons B(g) + C(g)$; $K_{P_1} = x$ atm^2

$P_1 \quad P_1 + P_2$

$D(s) \rightleftharpoons C(g) + E(g)$; $K_{P_2} = y$ atm^2

$P_2 + P_1 \quad P_2$

$P_{Total} = P_B + P_C + P_E$

$= P_1 + P_1 + P_2 + P_2$

$= 2(P_1 + P_2)$

$= 2(\sqrt{x+y})$

$x = K_{P_1} = P_1 \times (P_1 + P_2)$

$y = K_{P_2} = P_2 \times (P_2 + P_1)$

$K_{P_1} + K_{P_2} = x + y = (P_1 + P_2)(P_1 + P_2)$

$x + y = (P_1 + P_2)^2$

$\sqrt{x+y} = P_1 + P_2$

(**) Case of Incomplete neutralisation b/w [W.A + S.B / S.A + W.B]

Case (a) equivalents of W.A > equivalents of S.B

Soln will have W.A + Salt in the container ; such soln are called **ACIDIC BUFFER**

Case (b) eq of W.B > eq of S.A

Soln contains W.B + Salt at the end of Rxn ; such soln is called BASIC Buffer.

Buffer soln:- soln in which negligible pH change is observed upon add^n of small amount of Acid or Base.

or

soln which resist change in pH upon add^n of small add^n of acid or Base.

Acidic Buffer:- Mixture of W.A + its salt from S.B or W.A + its Conjugate Base

eg (i) $CH_3COOH + \underbrace{CH_3COONa}_{(CH_3COO)_2Ca}$

CH_3COO^- (C.B of CH_3COOH)

(ii) $\underset{W.A}{HF} / \underset{C.B}{F^-}$ or $HF + CaF_2$ or $HF + KF$ or $HF + NaF$ ~~$HF + NH_4F$~~

(iii) $(H_2CO_3 + NaHCO_3)$ or $(\underset{W.A}{H_2CO_3} / \underset{C.B}{HCO_3^-})$

(iv) $(NaHCO_3 + Na_2CO_3)$ or HCO_3^- / CO_3^{2-} ⟹ Composition of Blood Buffer

(v) $HCN + NH_4CN$ ~~×~~

(vi) $HCN + NaCN$

$$CH_3COOH \rightleftharpoons \underbrace{CH_3COO^-}_{\text{Salt}} + H^+$$

$\tilde{C}$ — $C\alpha$; C

$$K_a = \frac{[CH_3COO^-]_{Salt}[H^+]}{[CH_3COOH]}$$

$$[H^+] = K_a \times \frac{[W.A]}{[C.B]_{Salt}} \Rightarrow -\log[H^+] = -\log K_a + \log\frac{[CB]}{[WA]}$$

$-\log[H^+] \rightarrow$ pH ; $-\log K_a \rightarrow$ pKa ; W.B / C.A

Q. 0.1M CH_3COOH ($pK_a = 4.7$) + 0.1M $(CH_3COO)_2Ca$; pH = ?

$$pH = 4.7 + \log\left(\frac{0.2}{0.1}\right)$$

pH Calculat^n of Acidic Buffer

eg $CH_3COOH + CH_3COONa$

$\alpha \ll 1 \Rightarrow$ due to CIE ; $C - C\alpha \approx C$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (W.E) ; $C\alpha$; $C\alpha$

$CH_3COONa \rightarrow CH_3COO^- + Na^+$ (S.E)

$$\Rightarrow K_a = \frac{[CH_3COO^-]_{Total}[H^+]}{[CH_3COOH]} = \frac{[CH_3COO^-]_{Salt}[H^+]}{[CH_3COOH]}$$

$$[H^+] = K_a\left[\frac{[CH_3COOH]}{[CH_3COO^-]_{Salt}}\right]$$

$$-\log[H^+] = -\log K_a - \log\frac{[CH_3COOH]}{[CH_3COO^-]_{Salt}}$$

$$\boxed{pH = pK_a + \log\frac{[CH_3COO^-]_{Salt}}{[CH_3COOH]}}$$

(**) [weak acid] remains almost same due to CIE

Common ion

Due to CIE, α of CH_3COOH ↓es

$$[CH_3COO^-]_{Total} = \left([CH_3COO^-]_{W.A} + [CH_3COO^-]_{Salt}\right) \approx [CH_3COO^-]_{Salt}$$

for Acidic Buffer

$$pH = pK_a + \log\frac{[C.B \text{ of } W.A]}{[W.A]}$$

or

$$pH = pK_a + \log\frac{[\text{Anion of Salt}]}{[W.A]}$$

Henderson-Hasselbalch Eqn

② Basic Buffer

↳ Mix of Weak Base + its salt from S.Acid

or

W.B + its Conjugate Acid

eg: i) $(NH_4OH + NH_4Cl)$ $(NH_3(aq))$ or $NH_3(aq) / NH_4^+$

ii) $NH_4OH + (NH_4)_2SO_4$

(**) pOH of Basic Buffer $= pK_b + \log \frac{[\text{Salt of W.B}]}{[\text{W.B}]}$ or $pOH = pK_b + \log \frac{[\text{C.Acid}]}{[\text{W.B}]}$

$\boxed{pH = 14 - pOH}$

↳ Henderson-Hasselbalch Eqⁿ.

Q. 100ml, 0.1M CH_3COOH ($pK_a = 4.774$) + 100ml, 0.1M CH_3COONa

pH of Soln = ?

Soln:- Acidic Buffer

mmoles of $CH_3COOH = 100 \times 0.1$

$[CH_3COOH]_{new} = \frac{100 \times 0.1}{\text{Total Vol}} = \frac{100 \times 0.1}{200} = \frac{1}{20} = 0.05\ M$

$[CH_3COO^-]_{salt} = [CH_3COONa]_{new} = 0.05\ M$

$pH = pK_a + \log \frac{[CH_3COO^-]_{salt}}{[CH_3COOH]} = 4.774 + \log \frac{0.05}{0.05} = \frac{1}{1}$

$\boxed{pH = pK_a} = 4.774$

③ Salt Buffer (It is a salt Soln formed by Complete neutralizatⁿ of W.A + W.B)

eg: CH_3COONH_4, NH_4CN, NH_4F, $(NH_4)_2CO_3$ etc.

(**) $\boxed{pH = 7 + \frac{1}{2}[pK_a - pK_b]}$

Q. find pH of Soln

1) 100ml, 0.1M CH_3COOH + 50ml, 0.1M NaOH ($pK_a = 4.774$)

2) $\frac{3}{4}$th of CH_3COOH is neutralised by NaOH

3) Half of CH_3COOH is neutralised by NaOH

(1) $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$

$\Rightarrow$ t=0: 10 mmole, 5 mmole, 0, –

−5, −5, +5

5, 0, 5

$[W.A] = [C.B]$

Acidic Buffer

$[CH_3COOH] = 5/150\ M$

$[CH_3COONa] = 5/150\ M = [CH_3COO^-]$

$pH = pK_a$

2) $\frac{1}{4}$th CH_3COOH remaining

$\frac{3}{4}$th CH_3COONa formed

$pH = pK_a + \log \frac{(3/4)}{(1/4)}$

$pH = 4.77 + \log 3$

$= 4.774 + 0.47$

3) $pH = pK_a$

4) 100ml, 0.1M CH_3COOH + 200ml, 0.1M NaOH

10mmole, 20mmole

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O(l)$

10, 20, 0, –

-10	-10	$+10$
0	10	10

$[NaOH]_{Strong} = \frac{10}{300}\,M$

$[CH_3COONa] = \frac{10}{300}\,M$

$[\bar{O}H]_{Total} = [\bar{O}H]_{NaOH} + [\bar{O}H]_{\text{Anionic hydrolysis of } CH_3COO^-}$ → negligible

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + \overset{\ominus}{O}H$

$Na^+ + H_2O \rightarrow X$

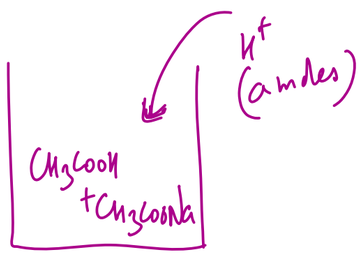
$[OH^-]_{Total} \approx [\bar{O}H]_{Strong\ Base} = \frac{10}{300} = \frac{1}{30}\,M$

$pOH = -\log\left(\frac{1}{30}\right)$

$pH = 14 - pOH$

Buffer Action

(I) Let few drops of strong acid (HCl) added to Acidic Buffer $(CH_3COOH + CH_3COONa)$



$\log\frac{[C.B]}{[W.A]} = \log\frac{[CH_3COO^-]}{[CH_3COOH]}$

$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$

C.B — added acid — W.A

$[C.B]\downarrow$, $[W.A]\uparrow$, $\frac{[C.B]}{[W.A]}$ ↓es

$pH = pK_a + \log\frac{[C.B]}{[W.A]}$ → ↓es

pH ↓es negligibly

(II) Small amount $\overset{\ominus}{O}H$ is added to $(HCN + CN^-)$ Acidic Buffer

pH ↑es negligibly $[HCN]\downarrow$, $[CN^-]\uparrow$

(III) Small amount of H^+ added to $(NH_4OH + (NH_4)_2SO_4)$ BASIC Buffer

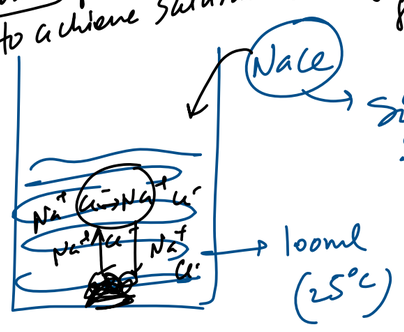
$pH\downarrow$, $pOH\uparrow$, $[NH_4OH]$ ↓es, $[NH_4^+]$ ↑es

(H.W) Example 13, 14, 15, 16 (P_g - 134, 135) → V.V. important

Solubility of Salt and K_{sp}

Very less soluble salt in H_2O called sparingly soluble salt

max amount of salt that can be dissolved to achieve saturation at a given T in given amount of solvent



NaCl (Saturated Soln) → Brine

$AgCl(solid) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$a - s$ mol/L, s, s

Solubility of Salt → Molarity

$K_{eq} = K_{sp} = [Ag^+][Cl^-]$

$K_{sp} = s^2$ (Solubility product)

$s = \sqrt{K_{sp}}$

(#) $A_xB_t \rightleftharpoons xA^{t+} + tB^{x-}$

$a - s$, xs, ts

$K_{sp} = [A^{t+}]^x[B^{x-}]^t = (xs)^x(ts)^t$

$K_{sp} = x^x t^t s^{(x+t)}$

(#) $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$

s, $2s$

s = solubility of $PbCl_2$

$K_{sp} = [Pb^{2+}][Cl^-]^2 = s \times (2s)^2 = 4s^3$

$s = \left(\frac{K_{sp}}{4}\right)^{1/3}$

$Al_2O_3 \rightarrow 2Al^{+3} + 3O^{2-}$